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On the constancy of the amount of lignin

Statistical analysis and kinetic study on the aging of wood (Part 1)

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Contents

Introduction

In this country, many of the aged structural timbers have been found in wooden buildings of Buddhist temples, among which is enumerated the oldest in the world, the Hôryû-ji Temple erected in the seventh century. The timbers have been preserved for many centuries without suffering from none of the biological agencies, such as wood-destroying fungi and insects, or agencies of severe nature, such as raining and direct sun-radiation. The changes in their properties with time are, however, covered frequently by the individual variations of wood and have attracted little attention of workers.

Miyoshi (*1*) reported the results of the chemical analyses and the tests of mechanical strengths using some of timbers of the Hôryû-ji Temple, and estimated the locality of the materials.

Kubo made a series of the observations on the chemical composition (*2*), mechanical strength (*3*), hygroscopicity (*4*), the degree of polymerization of the isolated cellulose (*5*), and X-ray diffraction pattern (*5*), with several specimens of a variety of ages of preservation obtained from the temple.

Recently, Kohara has made a collection over a wider range, which consists of about 150 specimens of the structural timbers and about 50 specimens of the unearthed woods, of various sources and species. In the course of his studies, the author came to collaboration with him, and the author's allotted task have been the application of statistical analysis and chemical kinetics

Kohara had named his object of studies as "aging". A green wood loses its water gradually when it is cut and reserved under the ordinary temperature and humidity, while the aging, which is often accompanied by desiccation, is an irreversible process different from the simple desiccation. The aged wood does not recover through absorption of moisture the characteristics which had been found in the green. It shows analogous trends to the heated wood, in spite of a wide difference in temperature and velocity of the change.

These resemblance and difference might be interpreted on the basis of chemical kinetics, and Kohara and the author were fortunate in becoming acquainted with the review of Stamm (*6*) on the reaction rates and activation energies of the thermal degradation of cellulosic materials, in the course of their comparative study of the aging in the ordinary temperature with the thermal degradation.

The thermal degradation or deterioration of wood is a complicated process as is seen among the great majority of the high polymeric materials. The aging at the ordinary temperature appears to be a slow thermal degradation (*7, 8*) and even some of the improvements in the properties are brought about by it, which are not generally conveyed in the terms, degradation and deterioration. At present, the main feature of the process are attributed to two factors, the degradation and the crystallization of cellulosic substances. Earlier reviews on these studies were undertaken by Kohara and the author (*9, 10*), and by Kohara (*8*).

The purpose of this series of reports is to systematize a statistical analysis of the data on the aging of wood, revising the estimates previously reported and adding new ones. In this paper, the emphasis is laid on the statistical examination on the hypothesis of the constancy of the amount of lignin, which has been assumed sometimes (*11, 12*) to interprete the data of chemical analyses on the aged materials obtained from natural sources. As the basis of this examinaiton, it includes also a determination of the reaction order and a statistical classification of the types of aging. In the subsequent papers the mechanism and the activation energy of the degradation, and the crystallization of cellulose would be dealt with.

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I. The materials and their sources

The materials have been collected by Kohara, and the details have been already reported (*8, 12-20*). On these materials, it is necessary, at present, to take two assumptions, namely, (1) each of them is a random sample under a given set of conditions, and (2) the set of conditions given for any material has been held constant over the whole period of its aging. One of the most effective methods to test these assumptions is thought to be the extraporation from the experiment at higher temperatures, while at the ordinary temperature the difficulties in sampling and the incompleteness of historical information are inevitable.

Species of the materials :- Table 1.1 gives the range of species of the materials, which covers seven species of softwoods and nine species of hardwoods. The rate of the degradation of cellulose is considerably larger in the hardwoods than in the softwoods, and the difference between them becomes obscure at higher temperatures (*21, 22*). The sign given to each of the materials indicates the species and the source simultaneously.

The classification of the sources :- The type and the rate of change in chemical composition of the wood in wet environment are significantly different from those in dry environment, as reported previously (*12*). The cellulose degrades rapidly and the extractives show little increment in ***wet*** environment. On the contrary, in ***dry*** environment the cellulose degrades slowly and the extractives increase remarkably. Hence, it is convenient to describe the former type of againg under the name of "W-type", and the latter "D-type". It is also found that the characteristics of some of the materials are classified into either of these types with difficulties, and these materials are classified to be under the ***miscellaneous*** conditions of aging. Thus, the sources of the materials are also divided into three groups, under the headings of W, D, and M.

W1, The Marshes of Satte-mura :- They are located in Aichi Prefecture (*20*). The specimens, four species of softwoods, S3W1, S1W1, S5W1, and S6W1, and four species of hardwoods, H4W1, H5W1, H6W1, and H7W1, have been found at a depth of about 2 meters, by Prof. S. Miki, of Osaka Municipal University, who discriminated the species and estimated the age of burial below 500 years.

W2, The Karako Sites :- Located in Nara Prefecture (*18*). The specimens, two species of softwoods and two species of hardwoods, were indebted to the Laboratory of Archaeology, of Kyoto University. The sites are of the 1st Century B. C., and is noted by the many wooden impliments unearthed. S5W2 is a vessel; S7W2, a bow; H1W2, a pounder; H6W2, a hoe. The late Dr. F. Onaka, of Kyoto University, discriminated the species.

W3, The Toro Sites :- In Shizuoka Prefecture (*8*). The sites were unearthed from the bottom of the River Abé, and the specimen, S4W3, had been a part of a fence in the ancient village, which had sunk under the water in the 1st Century B. C.

W4, The Tundra Districts in South Saghalien :- The specimens, S1W4, H2W4, and H9W4 had been unearthed by Prof. T. Yamasaki, of Kyoto Prefectural University, and distinguished by the late Dr. F. Onaka, who reported (*24*) the result of the observation on these specimens and those obtained from the Karako Sites, W2, under the microscope. He found that in the hardwoods cellulose was almost lost away from the secondary wall and it barely remained in the middle lamella and the primary wall, while in the softwoods the secondary wall seemed to be resistant, only showing some of enzymatically-produced cavities.

D1-16 The buildings of many centuries old :- These are located mainly in Kyoto and Nara. The nine specimens of Hinoki, a softwood, and eight specimens of Keyaki, a hardwood, have been selected from the collection of structural timbers of these sources. Their ages were estimated from their style of architecture, by the investigators in the field (*13-17, 19*). The static stress of a great diversity of directions and amounts might have produced rheological effects

Table 1.1 The distribution of species of the material.

Species	Material	
	Aged	Modern
Softwoods:		
Karamatsu (sp.), *Larix* sp.	S1W4	S1C1
Kôyamaki, *Sciadopitys verticillata*	S2M1, S2M4	S2C3, S2C4
Tsuga, *Tsuga Sieboldii*	S3W1	S3C1
Sugi, *Cryptomeria japonica*	S4W1, S4W3 ; S4M2, S4M5	S4C1, S4C2
Hinoki, *Chamaecyparis obtusa*	S5W1, S5W2 ; S5D2, 5, 6, 12-16 ; S5M3	S5C4, S5C2, S5C3
Nezuko, *Thuja Standishii*	S6W1	S6C1
Inugaya, *Cephalotaxus drupacea*	S7W2	S7C1
Hardwoods :		
Ibota, *Ligustrum obtusifolium*	H1W2	H1C1
Niré (sp.), *Ulmus* sp.	H2W4	H2C1
Keyaki, *Zelkowa serrata*	H3D1, 3, 4, 7-11.	H3C1, H3′C1.
Buna, *Fagus crenata*	H4W1	H4C1
Mizunara, *Quercus crispula*	H5W1	H5C1
Akagashi, *Quercus acuta*	H6W2	H6C1
Kuri, *Castanea crenata*	H7W1	H7C1
Han'noki, *Alnus japonica*	H8W1	H8C1
Yanagi (sp.), *Salix* sp.	H9W1	H9C1

Tabel 1.2 The age and source of the structural timbers.

Species		Age in years	Name of the temple	Localities
Hinoki	Keyaki			
	H3D1	240	Kan'non-ji	Kyoto Prefecture
S5D2		300	Nin'na-ji	Kyoto City
	H3D3	310	Enryaku-ji	Otsu City
	H3D4	320	Kiyomizu-dera	Kyoto City
S5D5		350	Tô-ji	Kyoto City
S5D6		350	Em'man-in	Otsu City
	H3D7	350	Nijô-jô (Castle)	Kyoto City
S5D8	H3D8	350	Kôdai-ji	Kyoto City
	H3D9	350	Hokke-ji	Nara City
S5M3	H3D10	530	Tômyô-ji	Kyoto Prefecture
	H3D11	650	Gokuraku-in	Nara City
S5D12		700	Renge'ô-in	Kyoto City
S5D13		730	Daihô'on-ji	Kyoto City
S5D14		900	Byôdô-in	Uji City
S5D15		1,200	Gokuraku-in	Nara City
S5D16		1,300	Hôryû-ji	Nara Prefecture

on them, but the differentiation of these effects is out of the scope of this paper. Table 1.2 gives a summary of the source of each specimen.

M1-5, The miscellaneous sources :- The description will be given in Chapter III.

The modern woods :- The recently cut woods corresponding to the aged materials have been obtained mainly from the Forest of Kyoto Prefectural University, except S4C2 and S5C2 obtained from Yoshino in Nara Prefecture; S2C3 and S5C3 from Kôya-san in Wakayama Prefecture, and S2C4 and S5C4 from Midono in Nagano Prefecture. The species of H3'C1 is Tsuki, ***Zelkowa serrata*** var. ***stipulacea*** Makino, which is very similar to Keyaki, ***Zelkowa serrata*** (Thunb). Makino, and some of the aged woods might be of this species (*14*). These exceptions may possibly improve the correspondence to the aged wood.

The "effective" temperature of the environment :- Since the rate of the chemical change increases exponentially with temperature, the effect of the temperature is ascribed not only to its average, but to its variation. Under the variation of temperature of the environment, the average rate constant over time, k_e, is defined as

$$k_e = (1/t)\int_o^t k\ dt, \tag{1.1}$$

where, k is rate constant at time t.

Frequently the relationship between the amount of reactant and the time is given by the differential equation capable of separation of the variables. Then the extents of the advancement of reaction in the same time interval under the variation of temperature and under the constant temperature at which the rate constant is equal to k_e in eq.(1.1) are equal to each other. It is convenient to name this constant temperature as "effective" temperature. Therefore, the effective temperature, T_e, is given in the equation,

$$k_e = Z\ \exp\ (-\Delta H/RT), \tag{1.2}$$

where, Z is the frequency factor and ΔH is the activation energy of the Arrhenius equation for the rate constant.

The effective temperature is not necessarily equal to the average temperature, T_o, and usually higher than T_o. If the rate constant at T_o is represented by k_o, the ratio of k_e to k_o is given by

$$\begin{aligned} k_e/k_o = 1 &+ (A^2/2 - A)\int_0^t \{(T-T_o)/T_o\}^2 dt \\ &+ (A^3/6 - A^2 + A)\int_0^t \{(T-T_o)/T_o\}^3 dt \\ &+ (A^4/24 - A^3/2 + 3A^2/2 - A)\int_0^t \{(T-T_o)/T_o\}^4 dt + \cdots\cdots, \end{aligned} \tag{1.3}$$

where, $A = \Delta H/RT_o$.

The variation of the atmospheric temperature might be expressed in terms of the Fourier series,

$$T = T_o + \sum_i (F_i/2)\ \sin\ (2t/a_i + p_i). \tag{1.4}$$

If the range of t in consideration is much larger than a_i's, eq. (3) combined with cq. (4) yields

$$\begin{aligned} k_e/k_o = 1 &+ (1/16)(A^2 - 2A)\sum_i (F_i/T_o)^2 \\ &+ (1/1924)(A^4 - 12A^3 + 36A^2 - 24A)\sum_i (F_i/T_o)^4 + \cdots\cdots. \end{aligned} \tag{1.5}$$

Therefore, the effect of the temperature on the rate of reaction is composed of the effect of the average temperature and the effect of the variations, for examples, diurnal and annual, which is approximately proportional to the sum of squares of the ranges and to the square of the activation energy.

Table 1.3 gives the estimation of the effective temperature by applying the above relationships to the meteorological data (24), and by assuming the activation energy to be about 25 kcal/mole as previously reported (22). It is of interest that the effective air temperature is higher than the effective ground temperature, while in the average the air temperature is lower than the ground temperature.

It is also concluded that the effect of the diurnal variation on the difference between the effective and the average temperatures on the earth is about one-fifth of that which is due to the annual variation. Since the annual variation is not moderated at all even in a building of such a type as Azekura-type (25), in which the temperature variation is thought to be reduced at most among the old buildings, the maximal range of the effective temperature and the rate constant may probably be about 1°C and one-fifth of the estimate respectively, due to the variety of extents of the depression of temperature variation in the structural timber.

The variations of longer periods are beyond the scope of this work, since they have not been known accurately.

II. The order of reaction and the rate constant of the loss in cellulosic substances.

The analytical data of aged specimens previously reported (12,17-20) are summarized and shown in Tables 2.1, 2.2, and 2.3, which include for comparison purposes parallel analyses of modern woods. The analyses were made according to the method of Government Forest Experiment Station, Tokyo, except that cellulose is determined by the method of Wise. Within the range of the materials, the decrease in cellulose content during the W-type aging covers almost the whole range of

Table 1.3 The effective temperatures in Kyoto, Nara, and their environs.

	Average Temperature	Range		Effective temperature	meteorological observatory
		Annual	Diurnal		
Air temperature	13.9°C	23.7°C	11.4°C	18.9°C	Kyoto
	14.3	22.9	10.4	19.0	Yagi[a]
Ground temperature (2m depth)	15.9	12.3	—	17.3	Kyoto
	16.2	9.0	—	16.9	Yagi[a]

[a] In Nara Prefecture.

degradation while it does only one-tenth or one-fifth of the original content during the D-type aging, as shown in Tables 2.1 and 2.2, respectively. If any appropriate method of correction for the gain or loss in weight is known, the data on the W-type aging allow us to determine the order of reaction.

Among the major components of wood, lignin is one of the most inert materials and the rate of alteration in amount during the W-type aging is less than one-fifth of that of cellulose, as discussed in Chapter IV. Then, the amount of cellulose relative to that of lignin is a convenient

Table 2.1 The chemical composition of the aged woods of W-type.

Material	Extractives			Holo cellulose	Alpha-cellulose	Pentosans	Lignin
	Alcohol-benzene	Hot water	1 %-NaOH				
	%	%	%	%	%	%	%
S3W1	1.95	2.91		62.46	45.11		34.58
S3C1	2.83	4.14		70.11	49.28		31.06
S4W1	0.83	1.03		67.41	49.97		32.04
S4C1, 2	4.46	4.14		69.10	46.62		33.18
S5W1	2.35	1.71		58.71	39.19		38.53
S5C4	2.77	3.02		64.64	48.07		29.83
S6W1	1.47	2.32		58.74	41.12		39.21
S6C1	5.00	6.57		65.87	46.43		30.87
S5W2	15.79	19.00	32.90	32.32	22.86	6.62	47.62
S5C3	2.77	3.02	10.51	64.64	48.07	8.95	29.83
S7W2	3.05	6.71	20.01	40.43	28.36	7.32	44.48
S7C1	2.96	4.02	11.24	67.78	41.57	9.54	31.46
S4W3	1.79	2.38	14.47	49.86	36.14		47.74
S4C1, 2	4.46	4.14	13.26	69.10	46.62		33.18
S1W4	4.42	5.94	13.70	37.21	29.89		56.91
S1C1	3.23	6.37	15.96	65.42	45.46		30.12
H4W1	6.90	7.81		49.46	32.29		32.24
H4C1	2.35	3.06		69.84	41.15		23.04
H5W1	2.47	4.06		56.60	38.53		37.00
H5C1	2.72	5.83		73.56	42.33		24.16
H7W1	3.65	8.38		49.87	35.81		32.81
H7C1	3.28	9.79		68.54	36.36		26.03
H8W1	7.74	7.61		51.18	34.71		33.29
H8C1	2.65	4.32		74.70	38.74		24.95
H1W2	3.97	4.96	23.01	4.82	2.83	5.94	62.82
H1C1	8.93	13.37	28.91	61.56	35.05	11.66	23.11
H6W2	8.94	6.38	38.99	7.86	4.18	6.42	60.61
H6C1	4.58	5.49	24.81	66.76	45.78	10.48	27.86
H2W4	3.28	5.36	24.87	12.91	7.49		78.07
H2C1	2.55	3.01	18.24	69.08	39.00		24.24
H9W4	5.19	13.82	27.51	11.30	6.50		64.45
H9C1	4.93	4.12	22.13	67.24	38.02		23.28

Table 2.2 The chemical composition of the aged woods of D-type.

Material (age in years)	Extractives			Holo-cellulose	Alpha-cellulose	Pentosans	Lignin
	Alcohol-benzene	Hot water	1 %-NaOH				
	%	%	%	%	%	%	%
S5C4	2.77	3.02	10.51	64.64	48.07	8.95	29.83
S5D5 (350)	5.97	6.22	13.76	64.97	47.45	8.81	32.59
S5D6 (350)	5.83	5.41	18.88	63.17	44.80	8.38	28.67
S5D13 (730)	9.75	4.95	24.44	62.60	45.73	9.42	29.79
S5D14 (900)	5.90	6.18	18.55	62.42	44.68	9.37	31.15
S5D15 (1200)	8.09	7.70	24.33	62.07	44.90	8.52	29.45
S5D16 (1300)	6.82	8.20	21.71	57.03	43.44	7.63	29.92
H3C1	9.32	5.66	24.11	65.07	40.98	13.66	22.46
H3D1 (240)	9.08	8.22	27.90	63.44	40.78	11.87	23.02
H3D4 (320)	11.09	10.41	37.56	53.06	33.78	12.88	23.56
H3D7 (350)	9.31	8.45	33.12	61.06	36.98	11.71	22.52
H3D9 (350)	12.62	12.78	32.00	53.58	35.80	10.48	23.82
H3D10 (530)	12.84	12.52	32.30	57.12	35.07	11.04	24.42
H3D11 (650)	14.75	10.98	40.56	53.64	30.82	12.94	23.95

Table 2.3 The chemical composition of the woods aged under miscellaneous environment.

Material (age in years)	Extractives			Holo-cellulose	Alpha-cellulose	Pentosans	Lignin
	Alcohol-benzene	Hot water	1 %-NaOH				
	%	%	%	%	%	%	%
S2M1 (1600)	29.22	8.69	25.37	43.91	31.37	6.59	27.83
S2M4 (20)	6.19	3.88	14.95	59.41	41.63	—	31.58
S2C3, 4	15.02	7.23	17.76	62.68	43.30	7.40	29.26
S4M2 (?)	3.73	4.25	11.57	61.39	35.11	10.02	36.49
S4M5 (60)	10.77	11.70	21.21	61.95	42.81	8.05	33.84
S4C1, 2	4.46	4.14	13.26	69.10	46.62	10.83	33.18
S5M3 (530)	6.32	4.88	20.78	61.53	41.95	9.34	34.69
S5C4	2.77	3.02	10.51	64.64	48.07	8.95	29.83

approximation to the absolute value corrected for the loss in total weight. During the D-type aging, however, the estimation is not so successful. But, at present, the absolute amount of cellulose is taken to be directly proportional to the cellulose/lignin ratio by content, assuming the constancy of the amount of lignin under the both types of aging.

The order of reaction and the rate constant during the W-type aging are roughly estimated previously and reported by Kohara (*21*). In this chapter they are re-examined together with the data on the D-type aging.

The fraction of residual cellulose :- The fraction of residual cellulose in aged wood of any species is defined as

$$\frac{(\text{cellulose-content/lignin-content})_{\text{aged}}}{(\text{cellulose-content/lignin-content})_{\text{modern}}}.$$

Table 2.4.A gives the fractions of residual holocellulose and alpha-cellulose in the specimens of the W-type, classified by distinctions between softwoods and hardwoods and between ages of burial. Table 2.4.B gives the results of a statistical analysis of the variance of the fraction to test the

Table 2.4 The fractions of residual cellulose in the aged wood of W-type and the analysis of variance between them.

A. The fraction of residual cellulose.

Class	Age in years	Specimen	Fraction of residual cellulose		
			Holo	Alpha	Class mean
SW1	below 500	S3W1	0.800	0.822	0.809
		S4W1	1.010	1.110	
		S5W1	0.703	0.631	
		S6W1	0.702	0.697	
SW2, 3	2,000	S5W2	0.313	0.298	0.426
		S7W2	0.422	0.483	
		S4W3	0.501	0.539	
SW4	above 10^4	S1W4	0.301	0.348	0.324
HW1	below 500	H4W1	0.506	0.561	0.588
		H5W1	0.502	0.594	
		H7W1	0.577	0.781	
		H8W1	0.513	0.672	
HW2	2,000	H1W2	0.0288	0.0297	0.0386
		H6W2	0.0541	0.0420	
HW4	above 10^4	H2W4	0.0580	0.0594	0.0600
		H9W4	0.0607	0.0618	

B. The difference in the fraction of residual cellulose between individual specimens and between holo- and alpha-cellulose.

Source of estimate[a]	S. S.	D. F.	M. S.	
Between holo- and alpha-cellulose	0.0327	1	0.0327	$Fo=1.60$, $Pr.>0.10$
Between specimens	0.7664	14	0.0547	$Fo=2.67$, $Pr.<0.05$
Interaction	0.2865	14	0.0205	
(Total	1.0856	29)		

[a] The fractions within a class have been divided by the class mean.

differences between individual members within classes and between holocellulose and alpha-cellulose within members. The former difference is significant at 5% level, while the latter is not significant generally, except in the class HW1. The expected coefficient of variation of $\bar{f}$, the mean of the fractions between holo- and alpha-cellulose of each specimen, is about 15% within each class, in other words,

$$\text{var}\,[\log \bar{f}]=0.0547\times(1/2)\times(0.4343)^2=0.516\times10^{-2},\quad (\text{D.F.}=14). \tag{2.1}$$

This gives the internal estimate of the variance, and some of the external estimate will be given below.

The rate constants at each of the supposed orders of reaction: - The order of the reaction is supposed to be an integer, including zero. The class means of f in the classes SW1 and HW1 give negatively deviated estimates, since only an upper limit is known about their age of burial. Similarly, the class means in SW4 and in HW4 give positively deviated ones, and the class means in SW2, 3 and in HW2 the normal estimates. The results are shown in Table 2.5. A and Fig. 2.1. A.

Among these estimates, those from SW4 and HW4 have been corrected for the lower temperature of their environment, based on the maximal value of the estimated activation energy, 30 kcal/mole (22), and the annual average temperature, about 4°C, at a depth of 2m of the Meteorological Station of Shikuka (in the old name) near the Tundra District in South Saghalien

Table 2.5 Discrimination between the supposed orders of reaction for the loss in cellulose during W-type aging.

A. The inconsistency among the estimated rates

Source of estimate	k x10^4yr and its weight[a] under the supposed order of reaction: 0	1	2	3	Probability of the inconsistency underlined
Softwoods :					
SW1 (under)	3.8(0.22)	4.2	4.7	5.3	Less than 0.25
SW2, 3 (normal)	2.9(5.45)	4.3(2.18)	6.7	11.3	
SW4 (over)	10.8	18.0	33.	68.	
Hardwoods :					
HW1 (under)	8.2(1.96)	10.6	14.0	18.9	Less than 0.0025
HW2 (normal)	4.8(1237.)	16.3(21.2)	124.	1670.	
HW4 (over)	15.0	45.1	250.	2200.	

B. The variance of log $\bar{f}$ estimated from the difference between the hardwood/softwood ratios by rate constant from different sources.

Source of estimate	Supposed order of reaction: 0	1	2	3
Log (k_H/k_S) *and its weight*[a] :				
HW1 and SW1	0.33 (0.20)	0.40 (0.15)	0.47 (0.12)	0.56 (0.09)
HW2 and SW2, 3	0.22 (5.42)	0.58 (1.98)	1.27 (0.64)	2.17 (0.25)
HW4 and SW4	0.14 (4.26)	0.40 (1.09)	0.88 (0.30)	1.51 (0.11)
Weighted mean	0.19 (9.87)	0.51 (3.23)	1.07 (1.06)	1.68 (0.45)
$10^2 \times$ *var* [*log* $\bar{f}$] :				
External (D. F. = 2)	1.03	1.28	3.94	9.02
Internal (D. F. = 14)	0.516	0.516	0.516	0.516
F_0	1.99	2.48	7.64	17.5
Probability, *less than*			0.01	0.005

[a] Given in parentheses; based on the internal estimate of the variance of log $\bar{f}$, in eq. (2.1).

(25) and on the effective temperature shown in Table 1.3.

The error in the fraction of residual cellulose propagates to the estimate of rate constant, following the relations

$\delta \log k = -(\delta \log f) f/(1-f)$, for zero-order reaction,

$\delta \log k = -(\delta \log f)/2.303 \log f$, for 1st-order reaction,

$\delta \log k = -(\delta \log f)/(1-f)$, for 2nd-orderr eaction,

$\delta \log k = -(\delta \log f)/(1-f^2)$, for 3rd-order reaction,

…………………… ………………….

According to these relations, the statistical weights of the estimates in Table 2.5 have been calculated, on a basis of the variance of log $\bar{f}$ in eq. (2.1).

The inconsistency between the estimated rates :- Supposing zero-order of reaction, the normal estimate of rate constant is lower than the estimate which should be deviated negatively, with the softwoods as well as with the hardwoods. The difference between the estimates is tested

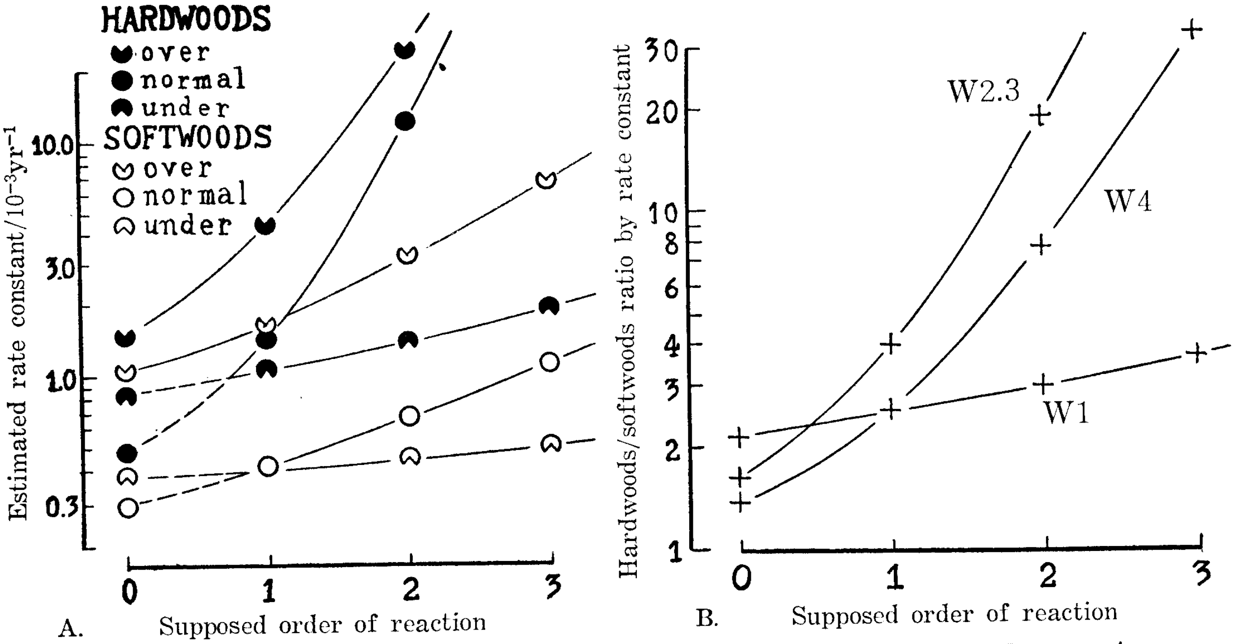

Fig. 2.1 Determination of reaction order of the loss in cellulose during W-type aging.

in a modified manner of the F-test for the difference of two means. In this case,

$$F_0 > (\log k' - \log k'')^2/(1/w' + 1/w'') \ \mathrm{var}\,[\log \bar{f}], \tag{2.2}$$

where, k's are the estimates of rate constant, and w's are the corresponding weights. Although the test is less efficient as compared with the ordinary test for the difference of two means, the reverse order of magnitude between the estimates on the hardwoods is significant at the 2.5% level.

The hardwoods/softwoods ratio by rate constant:- From the fractions of residual cellulose in the hardwoods and in the softwoods of the same age of burial, the ratio by rate constant between them is obtained without any exact knowledge about the length of age common to them both, as shown in Table 2.5.B and Fig. 2.1.B. The weighted variance of the estimated ratio within each of the triplicate classes different in the supposed order gives an external estimate of the variance of log $\bar{f}$, since there should be only one value of the true ratio for the triplicate.

The F-test shows that the variance within the triplicate under the assumption of second order is significant at the 1.0 percent level, as shown in Table 2.5.B. For the higher orders of reaction, the risk becomes higher, and the estimated rate constants and the ratio between them become more inaccurate.

The determination of the order of reaction:- On the basis of these tests, it is concluded that the assumption of the first order is the only one among integer order which involves no contradiction. Since any other possible case is more complicated as an interpretation of the data, it may be said that the loss in cellulose in the W-type aging is practically first order.

The above discussion has strictly established only that the decrease in the "cellulose/lignin ratio" is first order. This involves, however, the first-order loss in cellulose *per se*, as the simplest interpretaiton. If the cellulose content, C, and lignin content, L, of the aged material are supposed to satisfy the relationship,

$$C/L = (C_0/L_0)\exp(-kt), \tag{2.3}$$

where, t is time, k the first-order rate constant, and the suffix, 0, indicates the value of the modern wood, then the most simple interpretation of eq. (2.3) may be

$$C = C_0 \ \exp(-k't) \ \text{and} \ L = L_0 \ \exp(-k''t).$$

As the lignin content inecrases with time, k'' must be negative to fit the analytical data, and the negative value of k'' involves that the amount of lignin becomes larger than the total weight of the material in the later period of aging. To avoid this contradiction, the next trial may be

$$CW=C_0W_0 \exp(-k_Ct) \quad \text{and} \quad LW=L_0W_0 \exp(-k_Lt), \tag{2.4}$$

where W represents the total weight of the material. The former of the two equations shows the first-order loss in cellulose *per se*.

The first-order rate constant in the W-type aging: - Table 2.6 gives the first-order rate

Table 2.6 The first order rate constant of the loss in cellulose during W-type aging.

	Statistical[a] weight	Estimated value	
		original	adjusted[b]
$\log k_H \cdot yr$	21.2	-2.789	-2.793 ± 0.036
$\log k_S \cdot yr$	2.18	-3.370	-3.330 ± 0.112
$\log (k_H/k_S)$	3.23	0.510	0.537 ± 0.092

[a] Based on the internal estimate of the variance of $\log \bar{f}$, in eq. (2.1)

[b] For the probability of 95%; the error in the asumption of the constancy of the amount of lignin is neglected.

constants of the hardwoods and the softwoods and the ratio between them for the probability of 95%. The adjustment is undertaken to satisfy the geometrical relationship,

$$\log k_H - \log k_S = \log (k_H/k_S),$$

where k_H and k_S are the rare constant of the hardwoods and the softwoods respectively.

The sources of neglected error in the estimation of the rate constant are the error in the estimation of the age and the change in the amount of lignin with aging. The latter will be discussed in Chapter IV. The former yields an error below 2.5% with respect to the estimated rate, if the error of the age of SW2, 3 and HW2 is within ±50 years. This is negligible as compared with the error due to the variance of the fraction of residual cellulose.

The first-order rate constants in the D-type aging: - Fig. 2.2 shows the relation between aging time and the cellulose/lignin ratio of the timbers of Hinoki and Keyaki. Since the data are not enough to permit the determination of the order of reaction, the first order is assumed for convenience of comparison with the W-type aging. Table 2.7 gives the results of the analyses of variance to test the effect of the portion occupied by the material in the original timber and the effect of the difference in procedure of the chemical analyses on the rate constant. The data from the report of Kubo (2) have been added to Kohara's and the joint estimation has greatly improved the accuracy of the results on Hinoki.

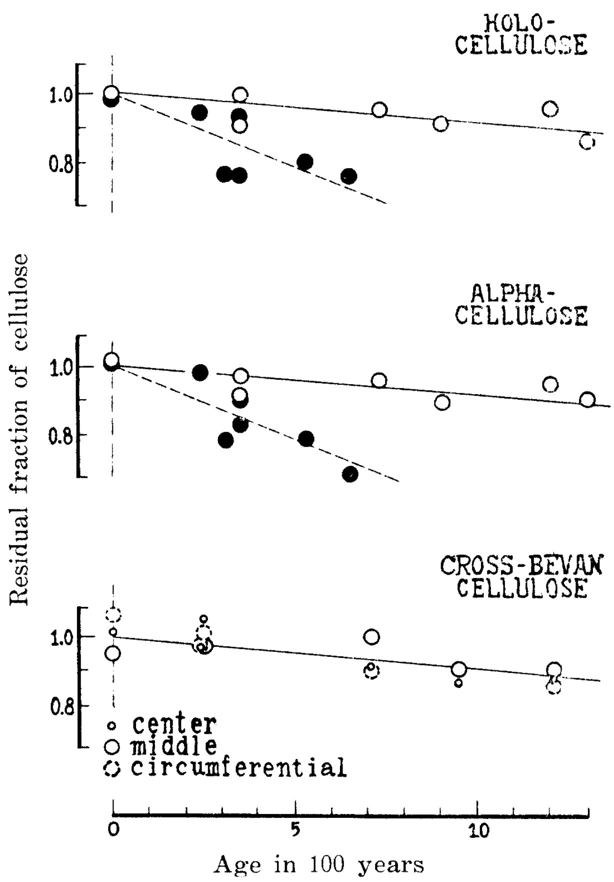

Fig. 2.2 Loss in cellulose on the basis of constant lignin during D-type aging. (closed circle--Keyaki; open circle--Hinoki).

The effects tested are not significant at all. The difference between the both species, however, is as remarkable as between the softwoods

Table 2.7 The first order rate constant of the loss in cellulose during D-type aging.

Regression equation supposed: log (C/L) = *const.* − 0.4343*kt*.

Source of estimate	S. S. 10^4	D. F.	M. S. 10^4	
Hinoki, max. age = 13 × 10^2*yr.*:				
Total corrected for mean regression	93.93	24	3.91	$k=(0.931\pm0.389)10^{-4}yr^{-1}$
Difference between Kohara's[a] and Kubo's[b]	12.42	1	12.42	$F_0=3.50$, Pr.> 0.05
Sum over Kohara's and Kubo's	81.51	23	3.54	
Within Kohara's corrected for classmean	33.50	11	3.04	$k=(0.579\pm0.564)10^{-4}yr^{-1}$
Between holo- and alpha-cellulose	0.14	1	0.14	$F_0=1/24.7$, Pr.> 0.25
Sum over holo- and alpha-cellulose	33.36	10	3.34	
Holocellulose	19.38	5	3.88	
Alpha-cellulose	13.98	5	2.80	
Within Kubo's corrected for class mean	48.02	12	4.00	$k=(1.243\pm0.539)10^{-4}yr^{-1}$
Between portions	18.87	2	9.44	$F_0=3.24$, Pr.> 0.05
Sum over portions	29.14	10	2.91	
Center	13.27	4	3.32	
Middle	12.19	3	4.06	
Circumferencial	3.68	3	1.24	
Keyaki, max. age = 6.5 × 10^2*yr.*:				
Total corrected for mean regression	109.58	11	9.96	$k=(4.66\pm2.22)10^{-4}yr^{-1}$
Between holo- and alpha-cellulose	4.47	1	4.47	$F_0=1/2.35$, Pr.> 0.10
Sum over holo- and Alpha-cellulose	105.11	10	10.51	
Holocellulose	65.16	5	13.03	
Alphaccellulose	39.95	5	7.99	

[a] The data are given in Table 2.2: Cellulose is determined by Wise method, using middle portion of the timber.

[b] Cross-Bevan cellulose.

and the hardwoods during the W-type aging.

Since the constancy of the amount of lignin is supposed here similarly to the W-type aging the obtained rate constants of the cellulose/lignin ratio are taken to be those of the cellulose ***per se***. The error of the assumption will be discussed in Chapter IV.

Comparison of the rate constants between the W-type and the D-type: - The obtained rate constants for the probability of 95% are summarized in Table 2.8. It is clear that the

Table 2.8 The first order rate constants of the degradation of cellulose during W-type aging and D-tyee aging, summarized[a].

Type of aging	Effectire temperature	Hardwoods	Softwoods
W-type	17°C	$(16.28\pm1.35)10^{-4}yr^{-1}$ (8 species)	$(4.68\pm1.21)10^{-4}yr^{-1}$ (6 species)
D-type	19°C	$(4.66\pm2.22)10^{-4}yr^{-1}$ (*Zelkowa serrata*)	$(0.93\pm0.39)10^{-4}yr^{-1}$ (*Chamaecyparis obtusa*)

[a] For the probability of 95%; the error in the assumption of the constancy of the amount of lignin is neglected.

degradation of cellulose is slower in the D-type aging than in the W-type aging.

Loss in pentosans :- Since the difference in residual fraction between holocellulose and alpha-cellulose is small, it is probable that the difference between holocellulose or alpha-cellulose and pentosans is also small.

The data on the D-type aging are not available to decide whether pentosans may decrease with a rate equal to cellulose or not, because of the narrow extent of advancement of aging and the much smaller amount of pentosans.

The data on the W-type aging show that the first-order rate constant of loss in pentosans is nearly equal to that of the loss in cellulose in softwoods, while the former seems to be somewhat less than the latter in hardwoods, as shown in Table 2.9.A.

Table 2.9 The first-order rate constant of loss in pentosans, k', compared with that of loss in cellulose, k, during W-type aging.

Scource of estimate	S. S. 10^2	D. F.	M. S. 10^2	
A. *Woods obtained from the Karako Sites, W2* :				
Total	4.140	3		
Difference between soft- and hard-woods	3.802	1	3.802	$F_0=22.5$, Pr. <0.05
Sum over softwoods and hardwoods	0.338	2	0.169	
Within sofwoods	0.192	1	0.192	$\log(k'/k)=-0.157\pm0.279$
Within hardwoods	0.146	1	0.146	$\log(k'/k)=-0.352\pm0.279$
B. *Woods of various sources summarized* :				
Overall corrected for overall mean	22.858	8		
Difference between soft- and hard-woods	12.873	1	12.873	$F_0=9.03$, Pr. <0.025
Sum over softwoods and hardwoods	9.985	7	1.426	
Total within softwoods	5.087	5	1.016	$\log(k'/k)=-0.061\pm0.115$
Between workers	2.760	1	2.760	$F_0=4.74$, Pr. >0.05
Sum over workers	2.327	4	0.582	
Within Kohara's	0.192	1	0.192	$\log(k'/k)=-0.157\pm0.150$
Within Gortner's	2.135	3	0.712	$\log(k'/k)=-0.013\pm0.106$
Total within hardwoods	4.898	2	2.449	$\log(k'/k)=-0.263\pm0.163$
Between workers	4.753	1	4.753	$F_0=32.6$, Pr. >0.10
Sum over workers	0.146	1	0.146	
Within Kohara's	0.146	1	0.146	$\log(k'/k)=-0.352\pm0.344$
Within Jahn-and-Harlow's	—	—	—	$\log(k'/k)=-0.085\pm0.487$

Comparison with the findings of others :- The above conclusion on the loss in pentosans is apparently confirmed by the joint estimation based on the data in Table 2.1 and those of Gortner (*11*) and Jahn and Harlow (*27*) on ancient woods, as shown in Table 2.9. B. However the difference obtained is accounted for by the higher values of fraction of residual pentosans of hardwoods found in Kohara's data only, thus additional observations are neccessary to establish the higher resistivity of pentosans in hardwoods.

The rate of loss in cellulose is obtained also from the above mentioned data of Gortner. They include the results of analyses of interglacial and preglacial woods buried in the earth for 4×10^4 years and 8×10^5 years respectively. In the former specimens the mean fraction between residual holocellulose and pentosans is 0.616, and in the latter the mean fraction is 0.103. These specimens had been subjected to the variation of temperature according to the advance and retreat of several glaciations. Supposing that the advancement of aging under ice sheet is negligible, the aging time of the interglacial specimens is thought to be about 2×10^4 years, since the latest glaciations began about 4×10^4 years ago and ended about 2×10^4 years ago according to Gortner.

If the loss in cellulosic substances is first order, the preglacial specimens are estimated to be 3.1 ± 1.4 times the interglacial ones as regards the total period of the glaciations retreating from them. The rate constant would be $(3.7\pm1.1)\ 10^{-5}\mathrm{yr}^{-1}$ taking only the variance of the mean fraction between residual holocellulose and pentosans into consideration. This corresponds to an effective temperature of 5 ± 4°C, neglecting the error in the estimation of the aging time and all the effects on the velocity of the degradation but that of the temperature of environment. These results of estimation might not be unreasonable, though it is difficult to check them at present.

III. The discrimination between the W-type and the D-type of aging based on the analytical data

This chapter deals with the change in amounts of the extractives and the change in total weight with aging on the constant lignin basis. The extractives in consideration are alcohol-benzene extract, hot-water extract and 1.0% sodium-hydroxide extract which were determined independently with each other. The total sum of the substances lost into or gained from the atmosphere or the subterranean water is indicated in the loss or gain in the total weight, which would be inversely proportional to the lignin content.

As a measure of the extent of advancement of aging, the loss in cellulose on the constant lignin basis is taken. Then the materials of unknown age and under complicated aging conditions are included in the scope, as well as the materials dealt in the previous chapter. The analytical data have been given in Tables 2.1, 2.2, and 2.3.

The preliminary and qualitative discussions on the subject except for the loss in total weight were given in the previous report(*12*).

Table 3.1. The gain in extractives compared with the loss in cellulose[a] during W-type aging.

Regression equation supposed: $X/L - X_0/L_0 = b(C_0/L_0 - C/L)$.

Source of estimate	S. S. 10^2	D. F.	M. S. 10^2	
Alcohol-benzene extract:				
Total corrected for mean regression	22.82	16	1.43	$b=-0.032\pm0.050$
Difference between soft- and hard-woods	1.38	1	1.38	$F_0=0.966$, Pr.>0.25
Sum over softwoods and hardwoods	21.44	15	1.43	
Within softwoods	9.77	8	1.22	$b=+0.011\pm0.104$
Within hardwoods	11.67	7	1.66	$b=-0.044\pm0.056$
Hot-water extract:				
Total corrected for mean regression	40.05	16	2.50	$b=-0.045\pm0.065$
Difference between classes	2.66	1	2.66	$F_0=1.06$, Pr.>0.25
Sum over classes	37.39	15	2.49	
Within softwoods	14.33	8	1.79	$b=+0.014\pm0.138$
Within hardwoods	23.06	7	3.24	$b=-0.062\pm0.074$
1.0%- sodium-hydroxide extract:				
Total corrected for mean regression	70.73	8	8.84	$b=-0.194+0.147$
Difference between classes	28.05	1	28.05	$F_0=4.60$, Pr.>0.05
Sum over classes	42.68	7	6.10	
Within softwoods	22.24	4	5.56	$b=+0.011\pm0.304$
Within hardwoods	20.44	3	6.81	$b=-0.257\pm0.168$

[a] Mean between holocellulose and alpha-cellulose.

The supposed regression equations: - Supposing linear regression between the gain in the extractives and the loss in cellulose, we obtain

$$X/L - X_0/L_0 = b(C_0/L_0 - C/L), \tag{3.1}$$

or,

$$X/L = a - b(C/L), \tag{3.2}$$

where, X, L, and C are the content of the extractives, lignin, and cellulose, respectively, and the suffix 0 indicates the value of the modern wood. The parameters, a and b, are assumed to be specific to each species.

As the content of cellulose, C, is taken the mean between the holo- and alpha-cellulose determined by Wise method or the content of Cross-Bevan cellulose, and the both are nearly equal to each other. If X's in eq.(3.1) and eq.(3.2) are taken to be equal to unity, the equations show a relationship between the gain in the total weight of the wood and the loss in cellulose.

The gain in extractives during the W-type aging: - Table 3.1 gives the relationship between the gain in the extractives and the loss in cellulose. The amount of alcohol-benzene extract and that of hot-water extract are nearly constant in the whole range of cellulose degradation. The

Table 3.2 The gain in extractives compared with the loss in cellulose[a] during D-type aging.

Regression equation supposed: $X/L = a - b(C/L)$.

Source of estimate	S. S. 10^4	D. F.	M. S. 10^4	
Alcohol-benzene solubles:				
Total corrected for mean regression	759.2	26	29.2	$b = +0.445 \pm 0.183$
Difference between Hinoki and Keyaki	97.1	1	97.1	$F_0 = 3.67$, Pr.> 0.05
Sum over Hinoki and Keyaki	662.2	25	26.5	
Within Hinoki	514.7	20	25.7	$b = +0.661 \pm 0.305$
Difference between Kohara's and Kubo's	2.1	1	2.1	$F_0 = 1/13.1$, Pr.> 0.10
Sum over Kohara's and Kubo's	512.7	19	27.0	
Within Kohara's	192.3	5	38.5	
Within Kubo's	320.4	14	22.9	
Within Keyaki	147.4	5	29.5	$b = +0.323 \pm 0.229$
Hot-water solubles:				
Total corrected for mean regression	639.7	21	30.5	$b = +0.434 \pm 0.200$
Difference between classes	17.6	1	17.6	$F_0 = 1/12.1$, Pr.> 0.10
Sum over classes	622.1	20	31.1	
Within Hinoki	391.2	15	26.1	$b = +0.549 \pm 0.373$
Difference between subclasses	6.6	1	6.6	$F_0 = 1/4.18$, Pr.> 0.05
Sum over subclasses	384.6	14	27.5	
Within Kohara's	41.1	5	8.22	
Within Kubo's	343.5	9	38.2	
Within Keyaki	231.0	5	46.2	$b = +0.387 \pm 0.237$
1.0%-sodium-hydroxide solubles:				
Total corrected for mean regression	3147.3	23	136.8	$b = +1.057 \pm 0.403$
Difference between classes	342.7	1	342.7	$F_0 = 2.69$, Pr.> 0.10
Sum over classes	2804.6	22	127.5	
Within Hinoki	1640.3	17	96.5	$b = +1.481 \pm 0.685$
Difference between subclasses	54.3	1	54.3	$F_0 = 1/1.83$, Pr.> 0.25
Sum over subclasses	1586.1	16	99.1	
Within Kohara's	824.2	5	164.8	
Within Kubo's	761.8	11	69.3	
Within Keyaki	1161.2	5	232.8	$b = +0.832 \pm 0.499$

[a] The mean between holocellulose and alpha-cellulose.

1.0%-sodium-hydroxide extract shows a slight loss. The differences in the regression coefficient between the softwoods and the hardwoods are not significant.

The gain in extractives during the D-type aging:- Table 3.2 gives the relationship between the gain in the extractives and the loss in cellulose in the specimens of Hinoki and Keyaki, and the additional data are obtained from the report of Kubo (2). The amount of alcohol-benzene solubles as well as well as the amount of hot-water solubles increase by one-half of the loss in cellulose. The increment of 1.0%-sodium-hydroxide extract is nearly equal to the loss in cellulose.

The effect of the portion in original timber from which the materials were obtained, the effect of the difference in the method of isolalation of cellulose, and difference between the species of Hinoki and Keyaki are not significant at all.

The loss in weight during the W-type aging:- Table 3.3 gives the relationship between the loss in cellulose and the loss in total weight. It is seen that the loss in weight is somewhat

Table 3.3 The loss in weight compared with the loss in cellulose[a] during W-type aging.

Regression equation supposed : $1/L - 1/L_0 = b(C_0/L_0 - C/L)$.

Source of estimate	S. S. 10^2	D. F.	M. S. 10^2	
Total corrected for mean regression	23.14	16	1.45	$b = -1.141 \pm 0.083$
Difference between soft- and hard-woods	2.51	1	2.51	$F_0 = 1.82$, Pr.> 0.10
Sum over softwoods and hardwoods	20.63	15	1.38	
Within softwoods	9.90	8	1.24	$b = -1.074 \pm 0.136$
Difference between subclasses	0.05	1	0.05	$F_0 = 1/25.2$, Pr.> 0.10
Sum over subclasses	9.85	7	1.41	
SW1 and S4M2	5.63	4	1.41	weighted by 1.000
SW2, 3, 4	4.22	3	1.41	weighted by 0.509
Within hardwoods	10.73	7	1.53	$b = -1.181 \pm 0.104$
Difference between subclasses	2.28	1	2.28	$F_0 = 1.62$, Pr.> 0.10
Sum over subclasses	8.45	6	1.41	
HW1	4.22	3	1.41	weighted by 0.916
HW2, 4	4.22	3	1.41	weighted by 0.139

[a] Mean between holocellulose and alpha-cellulose.

Table 3.4 The loss in weight compared with the loss in cellulose[a] during D-type aging.

Regression equation supposed : $1/L = a - b(C/L)$.

Source of estimate	S. S. 10^4	D. F.	M. S. 10^4	
Total corrected for mean regression	52.23	25	2.09	$b = -0.652 \pm 0.491$
Difference between Hinoki and Keyaki	0.95	1	0.95	$F_0 = 1/2.25$, Pr.> 0.25
Sum over Hinoki and Keyaki	51.29	24	2.14	
Within Hinoki	46.68	19	2.46	$b = -0.867 \pm 0.819$
Difference between Kohara's and Kubo's	5.63	1	5.63	$F_0 = 2.47$, Pr.> 0.10
Sum over Kohara's and Kubo's	41.05	18	2.28	
Within Kohara's	11.08	5	2.21	
Within Kubo's	29.97	13	2.31	
Within Keyaki	4.60	5	0.92	$b = -0.532 \pm 0.614$

[a] Cross-Bevan cellulose or mean between holocellulose and alpha-cellulose obtained by Wise method.

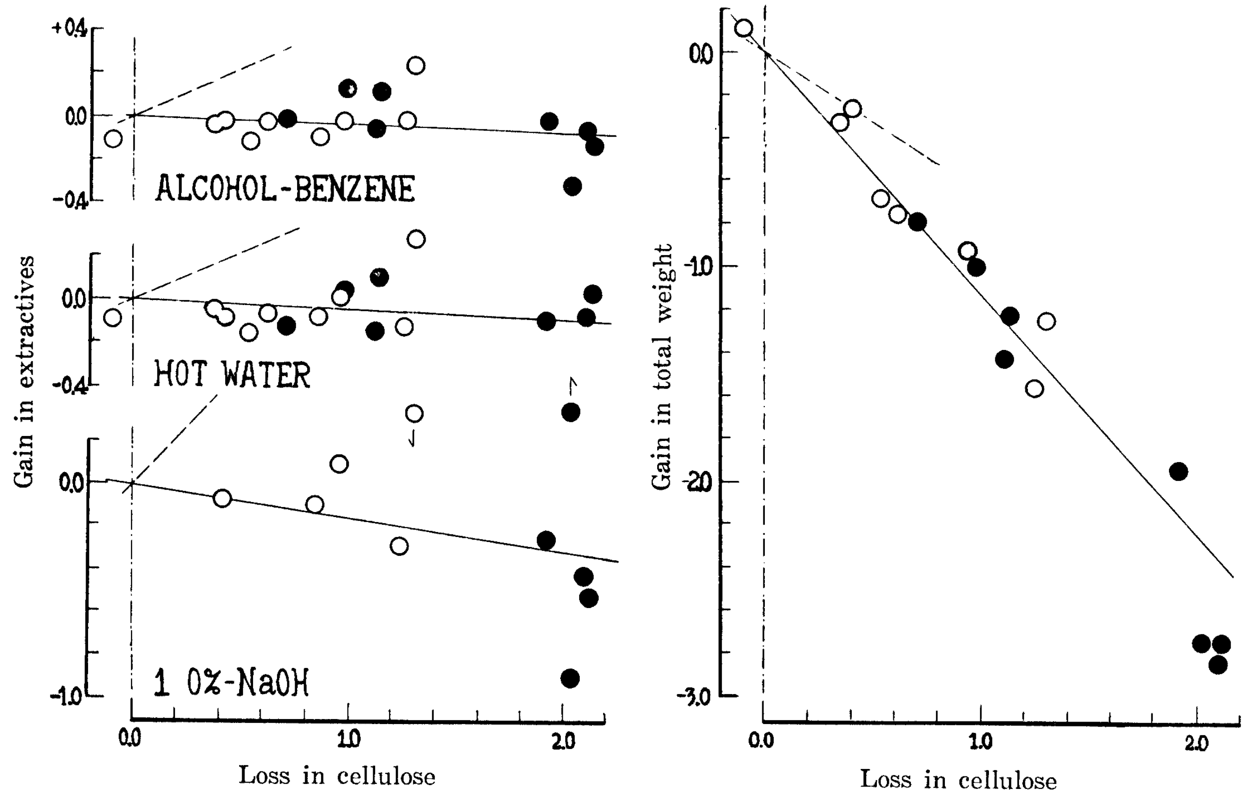

Fig. 3.1 The gains in extractives and total weight compared with the loss in cellulose, on the basis of constant lignin. (—— W-type: closed circle--hardwoods, open circle--softwoods; --- D-type)

larger than the loss in cellulose. Expressing this relationship in terms of the loss in holocellulose, the loss in weight is about 90% of the loss in holocellulose, since the loss in holocellulose is about 1.2 times in the softwoods and 1.3 times in the hardwoods as large as the loss in the mean between holocellulose and alpha-cellulose.

The residual variance of the regression seems to increase with aging, and the data have been weighted in proportion to the inverse of the residual variance in each subgroup of the materials of the nearly same degrees of aging. The difference in the regression coefficient, b, between the softwoods and the hardwoods is not significant, and the difference between the subclasses distinguished by degrees of aging is not significant.

The loss in weight during the D-type aging:- Table 3.4 gives the relationship between the loss in weight and the loss in cellulose in the timbers of Hinoki and Keyaki. The loss is evident, although the obtained regression coefficient is attended with a considerably large error. The effects of the various factors tested are not significant, compared with the error.

Comparison between the W-type and the D-type of aging:- The results obtained above on the ratios of the gains in the extractives and the total weight to the loss in cellulose are summarized in Fig. 3.1 and Table 3.5. The difference between the W-type and the D-type is significant, even in the loss in weight.

The material under the miscelleneous conditions of aging:- Table 3.6 gives the deviations of the gain-in-extractives/loss-in-cellulose ratio of the materials under miscellaneous conditions from the corresponding typical ratio, which has been shown in Table 3.5.

To normalize the deviations, they have been divided by the corresponding standard deviations. These normalized deviations are averaged within each material and the mean is normalized again by dividing by square root of three. Thus, the probability of the deviation of each material on the

Table 3.5 The gains in extractives and total weight compared with the loss in cellulose[a] (W-type aging, D-type aging, and findings of others are summarized).

Type of aging	Gain in extractives[b]			Gain in[b] total weight
	Alcohol-benzene	Hot-water	1.0%-NaOH	
W-type	-0.032 ± 0.050	-0.045 ± 0.065	-0.194 ± 0.147	-1.141 ± 0.083
(Spruce)[c]	-0.008 ± 0.033	——	——	-1.112 ± 0.189
(Beech)[d]	$+0.012$	——	——	-1.25
D-type	$+0.445\pm0.183$	$+0.434\pm0.200$	$+1.056\pm0.403$	-0.652 ± 0.491

[a] Mean between holocellulose and alpha-cellulose obtained by Wise method or Cross-Bevan cellulose.
[b] On the constant lignin basis; for the probability of 95%; the contents of extractives are determined independently with each other.
[c] Estimated from the data of Gortner (*11*); the holocellulose content is converted as
$0.82\times$(holocellulose content) $=1\times$(Cross-Bevan cellulose content).
[d] Calculated from the data of Jahn and Harlow (*27*).

whole is estimated approximately by reference to the table of the cumulative normal distribution function.

S2M1, Koya-maki unearthed from the Ishiyama Tomb:- The increase in the extractives is remarkable, as compared with such materials having been buried under the earth as mentioned above. The trends are rather similar to those of materials in the aging of D-type, although the increment of alcohol-benzene extract is significantly larger than the typical one. The old tomb is situated at the top of a hill, in Nara Prefecture, and the specimen is a part of a coffin which is thought to be intercepted from subtterranean water, by a thick wall of clay (*12*). On the contrary, the specimens from the sources classified under the headings from W1 to W4 have been in contanct with the water. Therefore, it is probable that the increment of the extractives largely depends on the absence or presence of water.

S2M4, Koya-maki constituting a bottom of a bath-tab:- This was obtained from a dwelling-house in Kyoto City (*12*). The extractives have been lost to an extent that exceeds the typical loss by the W-type aging, affording a marked contrast with the specimen S2M1.

S4M2, Jindai-sugi:- The wood is usually unearthed from Shizuoka, Kyoto, and Fukui Prefectures and used for inside decoration of Japanese style. The specimen was obtained from a volcanic district in Shizuoka Prefecture (*12*). In the trends of the loss in extractives, it is very similar to the material in the W-type aging, and it seems that the volcanic action has not produced any effect which is known by the usual manner of chemical analyses. Hence, in Tables 3.1, 3.3, and 3.5, the data have been already added to those on SW1-4.

S4M5, Sugi in a special usage:- This has been used as a side board of the saké-cask which is heated twice every year in a brewery, in Kyoto City, to stop fermentation (*12*). The extractives, however, show an increase nearly equal to the typical one of the D-type aging, and suggest the infiltration of some of the soluble substances.

S5M3, Hinoki from the Tomyo-ji Temple:- This has been used as a structural timber of the main hall of the temple. The fraction of residual cellulose is nearly equal to the expected value for the W-type aging equal in age, and significantly lower when compared with the specimens from analogous sources, among which the oldest one of 1,300 years old, S5D16, shows the fraction of about 0.90. This specimen shows also abnormal loss in mechanical strength and piezoelectric constant, though any singular feature is seen in the appearence (*27*). The gain in the extractives is situated in the middle of the both types, and no clear classification of this specimen can be made.

These characteristics of this specimen might possibly attributed to tha leak in the roof, upon which the recent repairs have been made, or the use of the older materials at the erection about

Table 3.6 Normalized deviations of the gain in extractives under miscellaneous environment from the typical gains during W-type aging (upper line) and during D-type aging (lower line).

Material (age in years)	Fraction of residual cellulose	Extractives			Mean	Probability *less than*
		Alcohol-benzene	Hot water	1 %-NaOH		
S2M1 (1,600)	0.750	+4.61 +3.25	+0.54 −1.19	+1.32 −0.73	+3.74 +0.76	0.0002
S2M4 (20)	0.884	−2.50 −4.32	−0.73 −2.05	−0.31 −1.53	−2.04 −4.55	0.04 0.000006
S4M2 (?)	0.746	−0.16 −2.17	+0.07 −1.72	−0.00 −2.17	−0.05 −3.50	0.0005
S4M5 (60)	0.890	+1.59 +1.01	+1.45 +1.29	+0.89 +0.09	+2.27 +1.38	0.02
S5M3 (530)	0.785	+0.85 −0.87	+0.36 −1.21	+1.09 −0.72	+1.33 −1.62	

500 years ago, or both.

Comparison with the findings of others :- According to the analytical data of Gortner (*11*) and Jahn and Harlow (*26*) on ancient woods, the loss in total weight is nearly equal to the loss in cellulose and the amount of alcohol-benzene extract remains almost constant, as shown in Table 3.5. Therefore it is concluded that their materials, including softwood and hardwood, had been under the W-type aging.

IV. The constancy of the amount of lignin

Among the workers on the aging of wood, Kubo (2) concluded that the lignification advances with aging, based on the increase in content of lign in the structural timbers of Hinoki. On the contrary, Gortner (*11*) supposed that the amount of lignin is constant instead of the apparent increase in its content, in his discussion on the chemical composition of the spruce specimens of inter- and pre-glacial periods in Minesota. On the basis of this assumption, Kohara and the author (*12, 20*) tried some preliminary discussions on the subjects of the previous chapters.

Jahn and Harlow (*26*) demonstrated the constancy using the data on the chemical composition and density of ancient beech stakes, by assuming implicitly that the total weight of wood decreases in proportion to the density, dry-weight/wet-volume, in other words, the wet volume of the wood is constant. Kohara and the author (*12*) showed that the constancy offers a reasonable explanation of the difference in the change in the density, dry-weight/dry-volume, between hardwoods and softwoods during the W-type aging.

The heat-aging of wood gives the both cases of the increase and the decrease. For example, in the report of Mitchell *et al* (*28*) on the effect of heating, the increase is seen at all the temperatures examined in closed system, that is, at 110°, 160°, and 220°C, and at 220°C in open system; the decrease, at 110° and 160°C in open system. For the degradation of isolated lignin, the numerical values of the rate constant at 150°C and the activation energy have been given by Stamm (*6*), and the extraporation shows that at the ordinary temperature the rate constant becomes larger than that of isolated cellulose.

The purpose of this chapter is to deal with the accuracy of the hypothesis and the conclusion from it by a statistical examination of the analytical data, since the hypothesis is not verified quantitatively in the works cited above.

The experimental relationships between lignin content and celluolose content obtained in the previous chapters ;- Apart from the frame of hypotheses, the obtained experimental relations between lignin content, L, and cellulose content, C, are given in eq.(2.3) and eq.(3.1), that is,

$$C/L=(C_0/L_0)\ \exp(-kt), \tag{4.1}$$

and

$$1/L-1/L_0=b(C_0/L_0-C/L). \tag{4.2}$$

The former of the equations involves as one of the simplest interpretations, as mentioned in Chapter II,

$$CW=C_0W_0\ \exp(-k_Ct)\ \text{and}\ LW=L_0W_0\ \exp(-k_Lt). \tag{4.3}$$

In the population of the set of C and L in which the latter relation is held, it is concluded that the loss in weight is directly proportional to the loss in cellulose if the amount of lignin is constant. In the same population, however, the constancy is only an example among the more general relationship between LW and C when the proportionality of the loss in weight to the loss in cellulose is assumed. Thus, if

$$W-W_0=b'(C_0W_0-CW), \tag{4.4}$$

then, substituting eq. (4.2) into eq. (4.4),

$$\frac{LW}{L_0W_0}=\left(\frac{1+b'C_0}{1+bC_0}\right)\left(\frac{1+bC}{1+b'C}\right), \tag{4.5}$$

where, the amount of lignin, LW, is constant only if $b=b'$.

Another relationship between lignin content and cellulose content:- The equation (4.3), the first-order loss in cellulose and lignin, combined with eq. (4.4) gives another relation between C and L, without the hypothesis of constant lignin. Thus, substituting k_L/k_C by m,

$$\left(\frac{1+b'C_0}{1+b'C}\right)^{1-m}=\frac{L_0}{L}\left(\frac{C}{C_0}\right)^m, \tag{4.6}$$

or, by rewriting,

$$\begin{aligned}&\log(L)-m\ \log(C)-(1-m)\ \log(1+b'C)\\&=\log(L_0)-m\ \log(C_0)-(1-m)\ \log(1+b'C_0)=\text{constant},\end{aligned} \tag{4.7}$$

where the constant in the right hand side is specific to each of the species of wood.

In Table 4.1 are given the numerical values of the parameters, m and b', basing on the data

Table 4.1 The ratio of lignin to cellulose by the first-order rate constant of loss in weight (m) and the ratio of the gain in total weight to the loss in cellulose (b').

Material	m	b'[a]	Data
W-type aging[b]:			
Softwoods and hardwoods	-0.09 ± 0.15	-0.83 ± 0.19	Kohara (*8, 18, 20*)[c] and Kohara & Okamoto (*12*)[c]
Spruce	-0.04 ± 0.11	-0.90 ± 0.17	Gortner (*11*)[d]
D-type aging:			
Hinoki and Keyaki[e]	$-0.5_4\sim+0.3_3$	$-0.8_7\sim0.0$	Kohara (*17, 19*)[c]

[a] Value for holocellulose.
[b] Ranges of m and b' are for the probability of 95%, estimated according to the regression equation (4.6) or (4.7).
[c] The data are given in Tables 2.1, 2.2, and 2.3; holocellulose is determined by Wise method.
[d] Holocellulose is determined by the method of Ritter and Kurth.
[e] Range of b' is assumed; m is calculated using eq. (4.9).

on the W-type aging same as those dealt with in Chapter III, and on the data of Gortner (*11*). There is a remarkable agreement between the results.

The error of the assumption in the aging of W-type:-

On combination with eq. (4.2), the equation (4.6) yields

$$\left(\frac{1+b'C_0}{1+b'C}\right)^{1-m}=\frac{1+bC_0}{1+bC}\left(\frac{C}{C_0}\right)^m. \tag{4.8}$$

The cellulose content, C, is perfectly arbitrary in a certain range, so that for eq. (8) to hold, m and $b'-b$ must vanish. As the result, eq. (4.6) and eq. (4.2) are compatible with each other only if

$$m = k_L/k_O = 0,$$

and
$$b' = \frac{W - W_0}{C_0 W_0 - CW} = b = \frac{1/L - 1/L_0}{C_0/L_0 - C/L}.$$

Therefore eq. (4.6) is generally competant with eq. (4.2) for the experimental relationship between cellulose content and lignin content.

Since m is not significant in Table 4.1, and b' in Table 4.1 is nearly equal to b in Table 3.3 taking the difference in the measure of cellulose content into consideration, the compatibility has been established within the experimental error, and the hypothesis of the constancy of the amount of lignin is not rejected.

If the amount of lignin would not maintain the constancy rigidly, the first-order rate constant of loss in cellulose shown in Table 2.8 might be attended with a systematic error ranging from -20 to $+5\%$, according to the range of m in Table 4.1.

The eerror of the assumption in the aging of D-type :- The above procedure to estimate the change in the amount of lignin encountered the difficulty that the parameters in eq. (4.7) became unstable and mutually dependent, when applied to the aging of D-type. Probably this is due to the narrow range of the extents of the degradation.

In a range of small degrees of aging, the combination of eq. (4.3) with eq. (4.2) and eq. (4.4) yields

$$m \fallingdotseq C_0(b - b')/(1 + bC_0), \tag{4.9}$$

where b' is the true ratio of the gain in total weight to the loss in cellulose, as defined in eq. (4). The true ratio of the gain in the component X to the loss in cellulose, b_X, is given by

$$b'_X = b_X - m(b_X + X_0/C_0), \tag{4.10}$$

where b_X is the apparent ratio such as given in Table 3.2. on the basis of constant lignin.

If the weight of the material is held constant under the aging, then

$$b' = 0.$$

Since $b \fallingdotseq -0.6_5$ in Table 3.4 and $C_0 \fallingdotseq 0.5_4$ the overall mean between holocellulose and alpha-cellulose of Hinoki and Keyaki in Table 2.2, substitution of these value into eq. (4.9) gives

$$m \fallingdotseq -0.5_4$$

This value of m involves that the rate constant of loss in cellulose is less than the value on the constant lignin basis by one-third, and the gain in 1.0%-sodium-hydroxide solubles is about three-halves of the loss in holocellulose. This gain roughly corresponds to the maximum yield of oxidation products of condensed phase. Since a smaller value of m gives an unexplicably larger gain in the extractives, these estimates might give one of the two limits of the interval of possible error.

Another limit is possibly given by supposing that the loss in weight does not exceed the one during W-type aging. At this limit, according to the estimates in Table 4.1,

$$b' \fallingdotseq -0.8_7, \quad \text{for holocellulose,}$$

then
$$m \fallingdotseq 0.3_3.$$

The rate constant of loss in cellulose is larger than the estimate on the constant lignin basis by about one-half.

These results are shown also in Table 4.1, to make a comparison with those on the W-type aging.

Summary

The analytical data on the woods aged at the ordinary temperature are examined by statistical method. The materials include the structural timbers of the ancient erection and the unearthed woods of various sources. At first the amount of lignin is assumed to be constant, then the assumption is tested. The results are as follows:

1) Two types of aging, named W-type and D-type, are capable of quantitative discrimination. The former is found in the wood in contact with water, mainly under the earth, and the latter is seen in the woods in dry environment. Under the intermediate humidity, woods might decay

in a short period by the attack of microorganism which is out of the scope of this paper.

The rapid degradation of cellulose and little or no alteration in the amount of the extractives are the characteristics of the W-type and a slow degradation of cellulose and remarkable increase in the extractives are the characteristics of the D-type. The numerical values of these characteristics are summarized in Tables 2.8 and 3.5, on the constant lignin basis.

2) The degradation of cellulosic substance and that of lignin during the aging of W-type are found to be first order with respect to the weight and for the degradation during the D-type aging the first order is only assumed.

The loss in total weight of wood is estimated to be roughly equal to the loss in cellulose (W-type), or speculated to be in a range from zero to the amount equal to loss in cellulose (D-type). The estimate of the rate constant of the loss in lignin ranges from -20 to $+5\%$ of that in cellulose (W-type), or from -50 to $+30\%$ (D-type).

Thus the difference between the apparent rate constant of loss in cellulosic substance on the constant lignin basis and the true one is within one-quater (W-type) or one-half (D-type) of the former. These systematic errors of the estimates are comparable to the accidental errors accompanied with the estimates.

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